

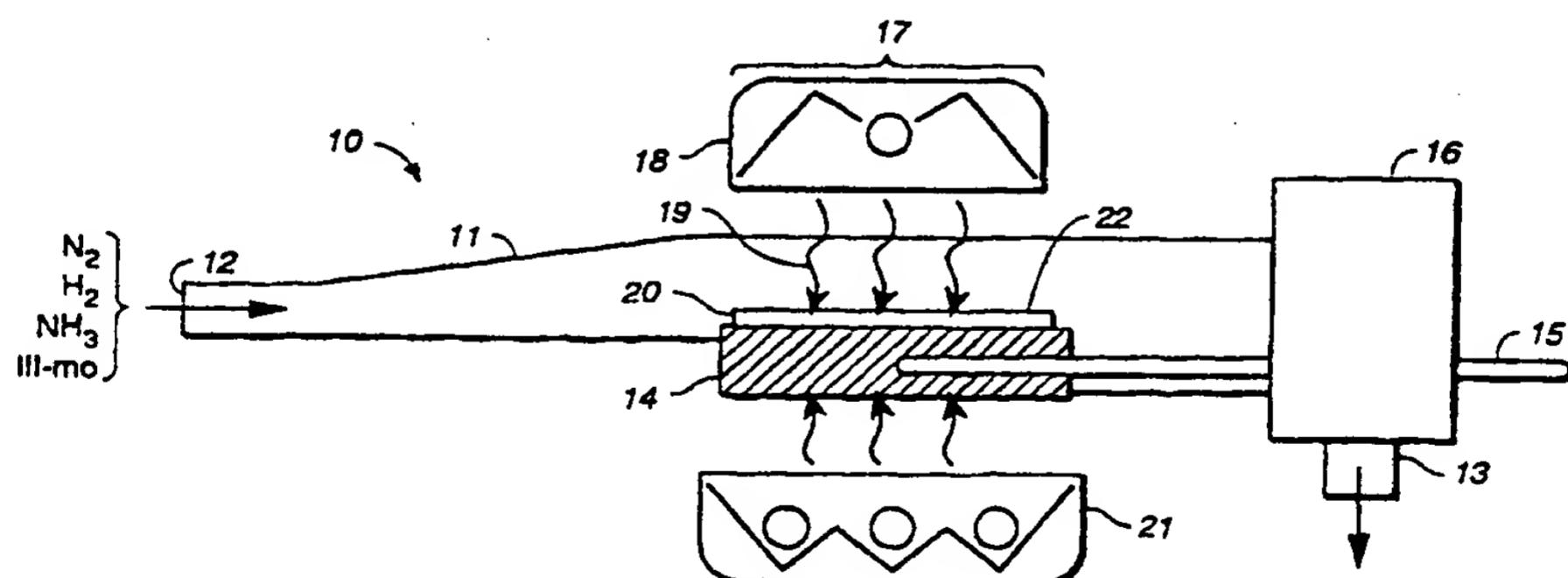
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :	A2	(11) International Publication Number:	WO 97/08356
C23C		(43) International Publication Date:	6 March 1997 (06.03.97)
(21) International Application Number:	PCT/US96/13188	(74) Agents:	PETERS, Howard, M. et al.; Peters Verny Jones & Biksa, L.L.P., Suite 6, 385 Sherman Avenue, Palo Alto, CA 94306-1840 (US).
(22) International Filing Date:	16 August 1996 (16.08.96)	(81) Designated States:	JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data:	08/516,527 18 August 1995 (18.08.95) US	Published	<i>Without international search report and to be republished upon receipt of that report.</i>
(60) Parent Application or Grant			
(63) Related by Continuation			
US Filed on	08/516,527 (CIP) 18 August 1995 (18.08.95)		
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(54) Title: MODIFIED METALORGANIC CHEMICAL VAPOR DEPOSITION OF GROUP III-V THIN LAYERS



(57) Abstract

The present invention relates to an improved apparatus for thin layer metal nitride crystal growth under metal organic chemical vapor deposition (MOCVD) conditions, which apparatus comprises: (1) a reaction cell comprised of quartz or other material capable of withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500 °C, which material transmits infrared radiation, when the reactor cell has: A) an inlet port for at least one volatile metalorganic compound; B) an inlet port for a nitrogen containing gas or a mixture of gases; C) a reaction zone for the metal nitride layer itself comprising a substrate upon which to deposit the metal III nitride, said substrate having a top surface and a bottom surface, and a susceptor to monitor the conduct and to control the temperature; (2) an infrared radiation source positioned immediately outside the reaction cell; (3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the group III nitride thin layer is formed, the bottom surface of the substrate is on the top of the susceptor which is heated by the lower radiant heat source; and (4) an outlet port. This apparatus produces films with useful properties by providing better control for thin film formation of the nitride, and is amenable to mechanization for less expensive mass production of films. The films are useful as semiconductors, LED, etc.

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MODIFIED METALORGANIC CHEMICAL VAPOR
DEPOSITION OF GROUP III-V THIN LAYERS

BACKGROUND OF THE INVENTION

Field of Invention

The present invention relates to an improved apparatus, configuration and method to deposit Group III-V thin films using modified metalorganic chemical vapor deposition (MOCVD). The improvement includes the use of an infrared radiation source coupled with a quartz reaction cell. This configuration allows direct heating of the substrate and the forming Group III-V compounds with greater control of the surface reactions and quality of the thin films which have improved properties. In particular, gallium nitride formed by this process shows improved properties.

Background and Related Art

Prior art in the MOCVD growth of III-V nitride thin films typically uses resistance heating or radio frequency (RF) heating. The state-of-the-art in nitride MOCVD has been reported by Nakamura et al (Applied Physics Letters, Vol 58, (#18), 6 May 1991). In Nakamura et al's approach, a two-flow vertical and horizontal MOCVD reactor is utilized to achieve high quality films as shown in attached Figure 4. A UV lamp is used in the vertical down-flow portion to help improve film quality. The vertical down flow serves to reduce the thermal boundary layer, but also allows the UV light to pass close to the surface through the N₂ and H₂ subflow gases before reacting with the Group-V hydride, e.g., NH₃, and Group-III alkyl (e.g., trimethylgallium, trimethylindium, or trimethylaluminum). This prior art reactor configuration does not scale-up well to mass production, and the gas flow patterns are complex and difficult to control. Other leading reactor designs that employ horizontal flow geometries typically use RF resistance heating. K. Hirosawa et al. (ref. Journal of Applied Physics, Vol. 32 (#8A), pp. L1039-L1042 (1 Aug. 1993)) employ a two flow reactor with heating. Direct radiant heating of the GaN wafer surface and susceptor is not presently employed by any of the leading manufacturers or reported in the literature.

Additional art of general interest includes:

S. Nakamura et al., in Applied Physical Letters, Vol. 64 (#13), p. 1677-1683 (28 March 1994) disclose the use of conventional MOCVD to produce candela-class high brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes.

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H. Amano, et al., in Japanese Journal of Applied Physics, Vol 29 (#2), pp. L205-L206 (Feb 1990) disclose the preparation of GaN film grown on sapphire by conventional metalorganic vapor phase epitaxy (MOVPE). The layer has room temperature stimulated emission near UV. This indicates the GaN film is promising as a UV laser diode.

Chemical vapor deposition (CVD) and metalorganic chemical vapor deposition (MOCVD) are known in the art.

10

Additional references of interest as background to assist one of skill in this art include U.S. Patent Numbers: 5,402,748; 5,379,720; 5,343,055; 5,305,341; 5,296,088; 5,268,039; US H 1264; 5,196,372; 5,179,042; 5,154,949; 5,141,893; 5,141,569; 5,106,453; and 5,082,798.

All references, patents, articles, standards, and the like cited herein are incorporated herein by reference.

15 It is therefore apparent that a need exists for an apparatus, configuration, and method to improve the quality of a Group III nitride and which method is amenable to scale-up for mass production. The present invention accomplishes these objectives.

SUMMARY OF THE INVENTION

20 The present invention relates to an improved apparatus for thin layer metal nitride, arsenide or phosphide crystal growth under metal organic chemical vapor deposition (MOCVD) conditions, which apparatus comprises:

25

(1) a reaction cell comprised of quartz or other material capable of withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500°C, which material transmits infrared and visible radiation, wherein the reaction cell has:

30

- A. an inlet port for at least one volatile metalorganic compound;
- B. the same or a different inlet port for a nitrogen, arsenic or phosphorus containing gas or a mixture of gases;
- C. a reaction zone for the formation of the metal nitride, arsenide, or phosphide layer, itself comprising:
 - i. a substrate upon which to deposit the metal III nitride, arsenide or phosphide wherein the substrate has a top surface and a bottom surface, and
 - ii. a susceptor to monitor the conduct and to control the

temperature;

- (2) an infrared radiation source positioned outside the reaction cell;
- (3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the Group III nitride thin layer is formed, and the bottom surface of the substrate is on the top of the susceptor which is heated by the lower radiant heat source, and;
- (4) an outlet port for reaction byproducts.

10 In one embodiment, the reaction cell comprises quartz.

In another embodiment, the infrared radiation source is a quartz halogen lamp.

15 In an additional embodiment, the nitrogen-containing gas or mixture of gases is selected from ammonia, nitrogen, hydrogen, hydrazine or combinations thereof.

The present invention also relates to an improved apparatus for thin layer

20 Group III metal nitride crystal growth under metal organic chemical vapor deposition (MOCVD) conditions, which apparatus comprises:

- (1) a reaction cell comprised of quartz or other material capable of withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500°C, which material transmits infrared radiation, when the reaction cell has:
 - (A) an inlet port for at least one volatile Group III metalorganic compound;
 - (B) the same or different port for a nitrogen containing gas or a mixture of gases;
 - (C) a reaction zone for the metal nitride layer itself comprising:
 - i. a substrate upon which to deposit the metal III nitride, wherein the substrate has a top surface and a bottom surface, and
 - ii. a susceptor to monitor the conduct and to control the temperature;
- (2) an infrared radiation source positioned outside the reaction cell;
- (3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the

Group III nitride thin layer is formed, and the bottom surface of the substrate is on the top of the susceptor which is heated by the lower radiant heat source; and

- (4) an outlet port.

5 In one embodiment, the reaction cell comprises quartz.
In another embodiment, the infrared radiation source is a quartz halogen lamp.
In an additional embodiment, the nitrogen-containing gas or mixture of gases is selected from ammonia, nitrogen, hydrogen, hydrazine, organic amines such as mono-, di- or tri-alkylamines or combinations thereof.

10

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic representation of the modified MOCVD apparatus having top and bottom radiant energy sources (e.g., radiant lamp heaters).

15 Figure 2 is a schematic representation of another modification showing jointly radio frequency or resistance heated reactor for MOCVD.

Figure 3 is a schematic representation of another embodiment showing an inverted configuration and multiple flow channel direct radiantly heated MOCVD.

20 Figure 4 is a schematic representation of the state-of-the-art two-flow MOCVD reactor as described by S. Nakamura in Applied Phys. Lett., Vol 58 (May 1991).

Figure 5 is a graph of a plot of luminescence intensity/a.u. versus wavelength in nm for the production of gallium nitride. The conventionally deposited layer without illumination as shown is (---). The improved layer produced according to the present invention is shown as (—).

25 Figure 6A is a graphic representation low temperature photoluminescence (PL) of GaN. Photochemical MOCVD increases band edge emission and reduces nitrogen vacancies through photo-catalysis of ammonia. Modified MOCVD growth uses high photon energy irradiation. Figure 6B shows standard GaN growth has nearly identical conditions with no light irradiation.

30 Figure 7A is a graphic representation of low temperature (22K) photoluminescence at low excitation ($P_{ex} = 200\text{mW/cm}^2$) from 2 microns of GaN grown by atmospheric pressure photochemical MOCVD or low pressure photochemical MOCVD films in the same reactor with the same growth rate V/III ratio. Photochemical MOCVD grown samples show extremely narrow band-edge emission (3meV) and no deep level.

Figure 7B is a graphic representation of strong visible band-edge PL from InGaN films with In compositions up to 20% by photochemical MOCVD at 700, 760 and 800°C.

Figure 8 is a graphic representation of quantum size effects and record linewidth photoluminescence has been obtained from $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ single quantum well (SQW) grown by photochemical MOCVD at 10, 20, 30 and 50Å. Because to large effective electron mass, the quantum size effects are obtained at thicknesses below 50Å.

Figure 9 is a schematic cross-sectional representation of the DH light emitting diode (LED).

Figure 10 is a graphic representation of electroluminescence intensity of $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ LED. The band-edge emission peak was at 390 nm and the donor-acceptor peak (450 nm) is only evident at low currents.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Definitions

As used herein:

"Alkyl" refers to all possible methyl, ethyl, propyl, butyl, pentyl or hexyl groups.

"Aluminum precursor compound" refers to volatile aluminum compounds, preferably alkyl and/or hydrogen substituted aluminum where alkyl has 1 to 6 carbon atoms. Trimethyl and triethyl are preferred.

"Arsenic precursor compound" refers to arlene or preferably alkyl substituted arsenic wherein alkyl has 1 to 6 carbon atoms. Tertiary-butyl arsenic is preferred.

"Boron precursor compound" refers to volatile boron compounds, such as diborane or alkyl substituted boranes where alkyl is 1 to 6 carbon atoms.

"Gallium precursor compound" refers to volatile gallium compounds. These include hydrogen and/or alkyl substituted gallium where alkyl is 1 to 6 carbon atoms.

"Group III elements" include boron, aluminum, gallium, and/or indium. Gallium is preferred. Combinations are also included.

"Group V elements" include nitrogen, phosphorus, and/or arsenic. Nitrogen is preferred. Combinations are also included.

"Indium precursor compound" refers to volatile indium compounds, preferably alkyl and/or hydrogen substituted indium, where alkyl has 1 to 6 carbon atoms.

"Nitrogen precursor compound" refers to ammonia, nitrogen, hydrogen, hydrazine, alkyl amines, or combinations thereof.

5 "Phosphorus precursor compound" refers to phosphine, phosphorus-hydrogen, preferably alkyl substituted phosphorus, wherein alkyl has 1 to 6 carbon atoms. Tertiary butyl phosphorus ($\text{CH}_3)_3\text{CPH}_2$ is preferred.

10 Although the following discussion focuses on the formation of nitrides, preferably gallium nitride, it is to be understood that gallium can be replaced with any other Group III element and also nitrogen can be replaced with arsenic or phosphorus, without departing from the present invention.

15 The current invention uses direct radiant heating of the growing gallium nitride film to improve the quality of the film. High power quartz-halogen lamps are used not only to heat the wafer surface directly, e.g., from the lower side, but to additionally catalyze the crystal growth reactions of the Group III alkyls with the group-V hydrides or organo-Group-V-precursors in a single-flow metalorganic chemical vapor deposition (MOCVD) reactor. A schematic of the reactor is shown in Fig.1. This arrangement allows for the lamps to directly illuminate the wafer and susceptor. The use of quartz-halogen lamps favors surface phase reactions over gas phase catalysis. This is due to the fact that the majority of the emission spectrum is in the IR to visible wavelengths.

20 At these wavelengths, the quartz wall and MOCVD precursor gases do not strongly absorb the radiation, but allow the radiation to pass to the gallium nitride surface. The close spacing of the lamps to the wafer surface ensures efficient heating and catalysis of the growing Group III (e.g., gallium nitride) thin film. A further improvement in this arrangement is the thermal and chemical desorption of wall deposits directly in front of the lamps. The separation of the IR or visible light source from the outer quartz surface is between about 0.5 and 3 mm, preferably about 1 mm.

25

30 This invention has widespread utility in depositing Group III (e.g., gallium nitride) thin films for electronic and optoelectronic applications. These materials are also used in the creation of blue and UV and full-color light emitting devices. These materials are also used in a wide range of solid-state electronic semiconductor devices.

The following description generally refers to Figures 1, 2, and 3. The present invention uses direct radiant illumination of the growing gallium nitride film and susceptor to improve the quality of the film. High power quartz-halogen lamps 18 are

used to catalyze the crystal growth reactions of the Group III alkyls with the group-V hydrides in a single flow metalorganic chemical vapor deposition (MOCVD) reactor 10, 40, or 70. The use of quartz-halogen lamps favors surface phase reactions over gas phase catalysis. The illuminated quartz-halogen lamp 18 is placed in close
5 proximity to the substrate and growing layer, e.g., within 0.1 to 1 inch of the exterior of reactor 11. This is due to the fact that the majority of the emission spectrum is in the IR to visible wavelengths. At these wavelengths, the quartz wall and MOCVD gases do not absorb the radiation, but allow it to pass to the gallium nitride surface. Use of shorter wavelengths (i.e., mercury lamps) of the art results in light being
10 absorbed in the gas phase. A schematic of the reactor is shown in Fig. 1. These arrangements allow for the lamps to directly heat the wafer located on the substrate and also the growing surface of the layer.

The best practice in employing the current invention is to ensure that high flux of radiant energy reaches the crystal surface. The radiant energy should also be of a
15 wavelength which catalyzes the desired reaction and is not strongly absorbed by the gas phase precursors.

Possible modifications of the current invention are shown in Fig. 2 and Fig. 3 below. A third flow of inert gas is used to keep the reactor walls free of deposits to ensure a high flux of radiation reaches the active surface (Fig. 3).

In a typical thin layer crystal deposition, the reactive gases enter cell 11 at inlet
20 12 and are conveyed to reaction zone 17 or 17A. The radiation 19 from light source 18 is directed to the top surface 22 (or the growing crystal layers) of substrate 20. The temperature of susceptor 14 is monitored by thermocouple 15 and controlled by a water cooler mount 16 and may be stationary or rotating. The bottom of substrate 20
25 is heated by heater 21. The reaction of the precursor gases occurs in zone 17 primarily at surface 22. The excess and/or byproduct gases exit at outlet 13.

Figure 2 shows an apparatus system 40 similar to Figure 1. However, the bottom of the susceptor 14 and substrate 20 is heated using radiofrequency (RF) or resistance heater 41.

Figure 3 shows a configuration 71 which is similar to Figure 1, except that reaction zone 17A is inverted, a rotating wafer holder 71 is present and multiple inlets 12, 12A and 12B are present for the gaseous reactants. The multiple inlets keep the reactants from premature contact and/or reaction prior to entering reaction zone 17A.

The apparatus and configuration includes cell (or reactor) 11 having a window

in the reaction path of quartz or a material which will not absorb infrared or visible light (between about 400 nanometers and 5 micrometers). The cell includes an inlet 12 for the metalorganic and nitrogen containing precursor gas or gases, an outlet 13 for the excess or byproduct gases, a susceptor 14, a thermocouple 15 to monitor the temperature, and a usually water cooled reactor mount 16 to control temperature.

5

The radiation is from any lamp source 18 which will produce the radiation of the required wavelength.

In reaction zone 17 or 17A, the radiant light source 18 is configured and focused to project the radiation 19 onto the surface of the substrate 20. The lamp or

10

light source 18 is positioned as close as possible to the quartz reactor 11. The bottom of the substrate 20 is heated, usually by a second radiant heat source 21.

The reactor cell may be either horizontal, vertical or any orientation.

The reactor cell may be both single-flow (Fig. 2) and two-flow and multi-flow geometry type (Fig. 3).

15

An inverted reactor minimizes thermal boundary layers as shown in Fig. 3.

In Figure 4, the horizontal MOCVD reactor 11 is used to achieve high quality films. Enclosure 50 protects the configuration from mechanical damage. Precursor metal organic compounds enter at inlet 12A. Precursor Group V compounds (such as NH₃, etc.) enter at inlet 12. An ultraviolet (UV) lamp 51 is focused in the vertical down-flow portion to help improve film quality. Susceptor 14 will rotate and is heated on the lower portion by heater 46. The gases react and form a thin layer on substrate 20. The unused or by-product gases exit at outlet port 13.

20

25

Preferably, the temperature of the deposition is between about 20 and 1400°C, more preferably between 100 and 1400°C, most preferably between about 400 and 1400°C.

Preferably the pressure of the deposition is between about 76 and 2000 torr, more preferably between about 700 and 1000 torr and most preferably between about 750 and 800 torr.

30

Preferably the mol ratio of Group III to Group V precursor is between about 1/10,000 and 2/1, more preferably between about 1/5000 and 2/1 and most preferably between about 1/1000 and 2/1, depending upon the stability of the Group V precursor.

The time of deposition varies based on the materials and thicknesses desired. Preferably the time is between 0.1 and 300 mins., more preferable between about 0.1 and 120 mins, or 5 to 60 min. One of skill in this art can determine from this

disclosure the temperature, time, pressure, radiation source, mol ratios of reactants, and specific reagents to produce the films having the improved properties.

The creation of the heterojunction InGaN LED is based upon the present advanced high-pressure photochemical MOCVD growth capability. The deep level state associated with nitrogen vacancies that is often problematic in low-pressure MOCVD is largely avoided with the present atmospheric pressure reactor design, which incorporates a high photon energy irradiation source. While not wanting to be bound by theory, the reduced nitrogen vacancies are believed to be achieved by photocatalyzed decomposition of ammonia by photons of sufficiently high energy as described in the equation below:

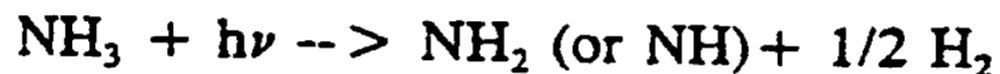


Figure 6A shows a comparison of photoluminescence (PL) from 2 μm of GaN grown under light irradiation, and Figure 6B shows unirradiated conditions in the same reactor under nearly identical growth conditions. Using this modified photochemical MOCVD approach, some of the highest reported bulk GaN electron mobilities have also been achieved. Values are as high as $720 \text{ cm}^2/\text{V.s}$ and $1200 \text{ cm}^2/\text{V.s}$ at 300K and 180K, respectively, have been obtained in GaN. In addition, photochemical growth coupled with high pressure MOCVD virtually eliminates the yellow band usually associated with nitrogen vacancies as shown in Figure 7A. Very strong band edge and weak deep level luminescence (which typically dominates) has been observed in GaN, $\text{Al}_{0.14}\text{Ga}_{0.86}\text{N}$, and in InGaN films (compare Figures 7A and 7B) grown using a modified atmospheric pressure approach.

InGaN quantum wells have been grown and have shown the narrowest reported room temperature photoluminescence linewidth 40meV (9nm) for a 50Å InGaN SQW as shown in Figure 8. It is crucial for viable lasers that double heterostructures be produced and high quality ohmic contacts are made.

Figure 9 shows results for our InGaN quantum well DH LED. Figure 9 is cross-sectional schematic representation of a light emitting diode 90 produced by the present invention. A substrate 91 (e.g. sapphire) has a thin layer of GaN (92)(or material having similar properties) as a low temperature buffer layer. The next layer is a 2 to 4 micron GaN-n buffer layer 93, which has on its top surface n-contact 94. On another portion of layer 93 is a GaN-n (Si) thin layer 95 having a thickness of between about 1000 and 10,000 Å (preferably about 5,000 Å). On top of the layer 95 is the DH LED quantum well 96 of indium-gallium-nitride (usually having a thickness

of about 150 Å). On the top surface of well 96 is a layer 97 of GaN-p (Mg) in a thickness of about 1,000 to 10,000 Å, preferably about 5,000 Å in thickness. On top of layer 97 is positioned p-contact 98 which is made up of nickel/gold.

This appears to be the first reported production of a double heterostructure (DH) InGaN/GaN LED in the U.S. For Fig. 9, the active region consists of a 150Å InGaN quantum well which emits strong band-edge emission at 20mÅ, and the blue-violet light is clearly visible in bright room light. In addition, a separate layer contact method (Ti evaporated and alloyed and then followed by Au) for n-type ohmic contacts to GaN. The result for the GaN of 0.4 ohm-mm and 3×10^{-6} ohms/cm² are currently record values.

The following Examples are presented for the purposes of explaining and describing the invention. They are not to be construed to be limiting in any manner.

General

The precursor reagents are available from chemical supply houses such as Morton International, Boston, Massachusetts; Aldrich Chemical Company, Milwaukee, Wisconsin; Eastman Kodak Chemical Company, Kingsport, Tennessee, and like others. The reagents must be of high purity to obtain the Group III-V crystal layer.

The MOCVD or CVD quartz reactor is available from commercial glass supply houses. The present quartz reactor was obtained from Thomas Swan & Co. Ltd., Cambridge, Great Britain.

EXAMPLE 1

DEPOSITION OF GaN

(a) The preparation of gallium nitride is as follows:

Epitaxial films are grown in a modified horizontal flow MOCVD reactor (Thomas Swan, Figure 1) operated at atmospheric pressure. C-plane sapphire is used as substrate. Trimethyl gallium (TMGa) and ammonia are used as precursors. Doping (n- and p-type) is accomplished by adding disilane and cyclopentadienylmagnesium (C_5H_5MgCl), respectively, to the gas mixture. After annealing the substrates in a hydrogen gas stream for 45 min at 1050°C using heating from the bottom and direct irradiation of the substrate surface from the top by the quartz-halogen lamp within about 2.5 cm (preferably about 1 mm) of the cell wall, the epitaxial growth is initiated by depositing a 190 Angstrom thick GaN nucleation layer at 600°C for 26 sec. The precursor injection amounts to 23.6 μ mol/min for TMGa. The injection of high purity ammonia, NH₃, amounts to 0.13 mol/min. The temperature is then raised to

temperatures between 1000 and 1080°C (1000°C in this example) to grow GaN of 1.2 μm thickness for 30 min. The TMGa injection is 23.6 μmol/min. During the entire growth procedure the substrate surface is irradiated with a conventional 1000 watt quartz halogen lamp from Ushio America, Inc. 10550 Camden, Cypress, California, 90630. The total gas flow into the reactor amounts to 6.3 liters/min.

For n-type doping 0.3 to 3.6 nmol/min disilane are injected, resulting in a n-type carrier concentration of up to $8 \times 10^{19} \text{ cm}^{-3}$. To achieve p-type doping in the films 0.9 nmol/min Cp₂Mg is added to the gas mixture resulting in a hole concentration of $1-2 \times 10^{17} \text{ cm}^{-3}$.

The direct irradiation of the substrate surface improves specifically the optical properties of the GaN films. An example of photoluminescence spectra obtained from two different films with and without surface illumination is shown in Figure 5. The units on the Y-axis are arbitrary units. The two curves when superimposed show I_b/I_d to be superior for the surface illumination layer between 500 and 650 nm. It is shown that the intensity of the broad luminescence band, I_d , at wavelengths around 550 nm is reduced in the low temperature and room temperature photoluminescence. An indicator for the optical quality of the films is the intensity ration I_b/I_d between the band edge luminescence, "I_b," and the deep level luminescence "I_d". At 22 K, I_b/I_d amounts to 4795 for GaN grown with surface irradiation and 268 for GaN grown without surface irradiation.

(b) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of a mixture of hydrogen and nitrogen gas, a corresponding gallium nitride layer having improved properties is obtained.

(c) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of methyl amine, a corresponding gallium nitride layer having improved properties is obtained.

(d) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of hydrazine gas, a corresponding gallium nitride layer having improved properties is obtained.

(e) Similarly, when Example 1(a) is repeated, except that the trimethylgallium is replaced with a stoichiometrically equivalent amount of trimethylindium, a corresponding indium nitride layer having improved properties is obtained.

(f) Similarly, when Example 1(a) is repeated, except that the trimethyl gallium is replaced with a stoichiometrically equivalent amount of a mixture of trimethyl aluminum, a corresponding aluminum nitride layer having improved properties is obtained.

5 (g) Similarly, when Example 1(a) is repeated, except that the trimethyl gallium is replaced with a stoichiometrically equivalent amount of a mixture of trimethylboron, a corresponding boron nitride layer having improved properties is obtained.

10 (h) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of tertiary butyl arsenic, a corresponding gallium arsenide layer having improved properties is obtained.

15 (i) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of tertiary butyl arsenic and trimethylgallium is replaced with a stoichiometrically equivalent amount of trimethyl indium, a corresponding indium arsenide layer having improved properties is obtained.

20 (j) Similarly, when Example 1(a) is repeated, except that the ammonia is replaced with a stoichiometrically equivalent amount of tertiary butyl phosphorus, and trimethylgallium is replaced with a stoichiometrically equivalent amount of trimethyl indium, a corresponding indium phosphide layer having improved properties is obtained.

25 (k) Similarly, when Example 1(a) is repeated, except that the trimethyl gallium is replaced with a stoichiometrically equivalent amount of a mixture of trimethylgallium and trimethyl indium, a corresponding indium gallium nitride layer having improved properties is obtained.

(l) Similarly, when Example 1(a) is repeated, except that the trimethylgallium is replaced with a stoichiometrically equivalent amount of a 50/50 (mol/mol) mixture of trimethylaluminum and trimethyl gallium, a corresponding aluminum gallium nitride layer having improved properties is obtained.

EXAMPLE 2

Production of Films to Form LED

All epitaxial films were grown in a modified horizontal flow MOCVD reactor shown in Figure 1 operated at atmospheric pressure (760 torr). The radiation source is a quartz-halogen lamp and is positioned directly above the wafer, in close proximity (about 1 mm) to the upper quartz wall, which also keeps the upper quartz wall hot

enough to desorb deposits and keep it clear and clean. C-plane sapphire was used as substrate. Trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia were used as precursors. N- and p-type doping were accomplished by adding disilane (Si_2H_6) and cyclopentadienylmagnesium (Cp_2Mg), respectively, to the gas mixture.

5 After annealing the substrates at 1050°C, the epitaxial growth was initiated by depositing a 190 Å thick GaN nucleation layer at 600°C. The temperature was then raised to 1080°C to grow GaN of 1.2 to 5 microns thickness. The 0.1 to 0.2 micron thick InGaN layers were grown on 4 microns thick n-GaN layers. The growth temperature of InGaN was varied between 650 and 800°C, and the input flows of
10 TMGa and TMIn were varied from 1.3 to 13 micromol/min and 1.9 to 24 micromol/min, respectively. After the InGaN layer deposition the temperature is raised to 1080°C again and trimethylgallium, ammonia, and Cp_2Mg are introduced into the reactor to grow the p-type film. The ammonia flow was kept constant at 0.12 mol/min. To increase the photoluminescence (PL) efficiency, the InGaN layers were
15 doped with silicon by adding 0.3 to 3.6 nmol/min disilane, resulting in a n-type carrier concentration of about $8 \times 10^{19} \text{ cm}^{-3}$. The epitaxial layer structure was then fabricated into a blue light emitting diode (LED) by depositing n-contacts (TiAl) and p-contact (NiAu) to the n-layer and p-layer, respectively. The time to produce the layers prior to depositing the p-contact and n-contact was rapid, between about 5 and 120 min.
20 The entire growth process for the layers is completed in about 1-2 hours with present equipment. Less time would be necessary with improved or large equipment.

While only a few embodiments of the invention have been shown and described herein, it will become apparent to those skilled in the art that various modifications and changes can be made in the improved apparatus or the improved method to deposit thin layers of Group III-V nitrides by metalorganic chemical vapor deposition (MOCVD) without departing from the spirit and scope of the present invention. All such modifications and changes coming within the scope of the appended claims are intended to be carried out hereby.
25

What is claimed is:

1. An improved apparatus for thin layer metal Group III-V crystal growth under metal organic chemical vapor deposition (MOCVD) conditions, which apparatus comprises:

(1) a reaction cell comprised of quartz or other material capable of 5 withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500°C, which material transmits infrared and visible radiation, wherein the reaction cell has:

- A. an inlet port for at least one volatile metalorganic compound of Group III;
- B. the same or a different inlet port for a nitrogen, arsenic or phosphorus containing gas or a mixture of gases;
- C. a reaction zone having top side irradiation of the metal III-V

layer itself comprising:

- i. a substrate upon which to deposit the metal III-V nitride, arsenide or phosphide wherein the substrate has a top surface and a bottom surface, and
- ii. a susceptor to monitor and a thermocouple to control the temperature;

(2) an infrared and visible radiation source positioned immediately 20 outside and adjacent to the reaction cell;

(3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the Group III-V thin layer is formed, and the bottom surface of the substrate is on the top of the susceptor which is heated by the lower 25 radiant heat source; and

(4) an outlet port for gases.

2. The apparatus of Claim 1 wherein the reaction cell comprises quartz.

3. The apparatus of Claim 1 wherein the infrared radiation source is a quartz halogen lamp, and is within 1 to 5 mm of the cell.

4. The apparatus of Claim 1 wherein the nitrogen-containing gas or mixture of gases of port B is selected from ammonia, nitrogen, hydrogen, hydrazine, alkyl amines or combinations thereof.

5. The apparatus of Claim 1 wherein the volatile Group III metal organic

compound of port A is selected from aluminum, gallium, indium or combinations thereof.

6. An improved apparatus for thin layer metal nitride crystal growth under metalorganic chemical vapor deposition (MOCVD) conditions, which apparatus comprises:

(1) a reaction cell comprised of quartz or other material capable of 5 withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500°C, which material transmits infrared radiation having;

A. an inlet port for at least one volatile Group III metalorganic compound;

B. an inlet port for a nitrogen containing gas or a mixture of gases;

C. a reaction zone for the metal nitride layer itself comprising:

i. a substrate upon which to deposit the metal III nitride, said substrate having a top surface and bottom surface,

ii. a susceptor to monitor the temperature, and

iii. a thermocouple to control the temperature;

(2) an infrared radiation source positioned outside the reaction cell;

(3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the Group III nitride thin layer is formed, the bottom surface of the substrate is on the top of the susceptor which is heated by the lower radiant heat source; and

(4) an exit port for gases.

7. The apparatus of Claim 6, in one embodiment wherein the reaction cell comprises quartz.

8. The apparatus of Claim 6, in another embodiment wherein the infrared radiation source is a quartz halogen lamp.

9. The apparatus of Claim 6, wherein the nitrogen-containing gas or mixture of gases is selected from ammonia, nitrogen, hydrogen, hydrazine, alkylamines or combinations thereof.

10. The apparatus of Claim 6, wherein the metalorganic of Group III of port A is selected from aluminum or indium.

11. An improved apparatus for thin layer metal nitride crystal growth under metalorganic chemical vapor deposition (MOCVD) conditions, which apparatus

comprises:

(1) a reaction cell comprised of quartz or other material capable of withstanding pressures of between about 1 and 10,000 torr, and a temperature of between about 0 and 1500°C, which quartz or material transmits infrared and visible radiation having;

- A. an inlet port for at least one volatile metalorganic compound of gallium;
 - B. the same or a different inlet port for a nitrogen containing gas or a mixture of gases;
 - C. a reaction zone for the gallium nitride layer itself comprising:
 - i. a substrate upon which to deposit the gallium III nitride, said substrate having a top surface and bottom surface,
 - ii. a susceptor to monitor the conduct, and
 - iii. a thermocouple to control the temperature;
- (2) an infrared radiation source positioned outside the reaction cell;
- (3) a lower radiant heat source, wherein the infrared radiation source is positioned to irradiate through one side of the quartz cell and heat directly onto the top surface of the substrate where the gallium nitride thin layer is formed, the bottom surface of the substrate is on the top of the susceptor which is heated by the lower radiant heat source; and

- (4) an exit port for gases.

12. The apparatus of Claim 11, wherein the reaction cell comprises quartz.

13. The apparatus of Claim 11, wherein the infrared radiation source is a quartz halogen lamp.

14. The apparatus of Claim 13, wherein the nitrogen-containing gas or mixture of gases is selected from ammonia, nitrogen, hydrogen, hydrazine, alkylamines or combinations thereof.

15. The apparatus of Claim 14 wherein the inlet ports are each configured to keep the reactive volatile gases separate until they reach the reaction zone.

16. An improved method to produce Group III nitride layers having improved physical, electrical and optical properties using the apparatus of Claim 1, which method comprises:

- (1) under metalorganic chemical vapor deposition conditions contacting

- (i) at least one volatile metalorganic compound of a Group III metal and;
 - (ii) a nitrogen-containing gas or a mixture of gases having a source of nitrogen in a reaction zone at between about 0 to 1500°C at a pressure of between about 76 and 2000 torr for between about 0.5 and 300 mins. wherein the substrate and surface of the growing crystal layer is irradiated and heated on the top of the apparatus and the growing crystal layer by a light source emitting infrared, radiation visible radiation or combinations thereof; and recovering the Group III nitride having improved properties.

10

17. The improved method of Claim 16 wherein the temperature is between about 500° and 1400°C and the separation of the top surface of the quartz reactor and the lower surface of the lamp is between about 1 to 5 mm.

18. The improved Group III nitride produced by the method of Claim 16.

19. The improved Group III nitride, arsenide, or phosphide produced by the method of Claim 16.

20. The improved Group III nitride produced by the method of Claim 16.

21. The improved gallium nitride, indium nitride, aluminum nitride or combinations thereof produced by the method of Claim 16.

22. The improved method of Claim 16 wherein the deposition of layers occurs in between about 60 and 120 min.

23. The improved method of Claim 16 wherein the temperature is between about 500° and 1400°C, the temperature is cycled through various temperature ranges, the volatile metal organic compound is a trialkylgallium, and the nitrogen-containing gas is ammonia.

24. The improved process of Claim 23 wherein trialkylindium is also present.

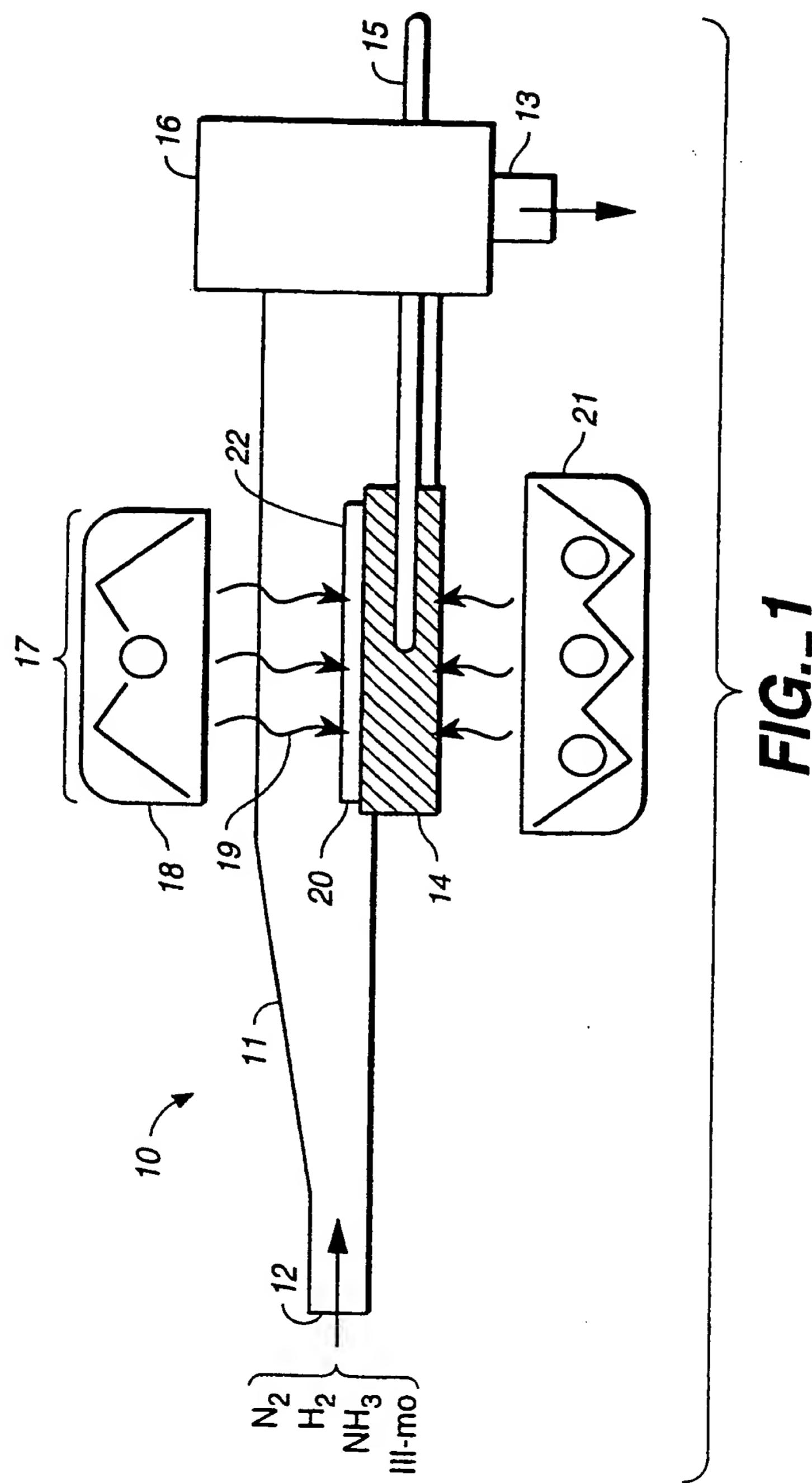


FIG. 1

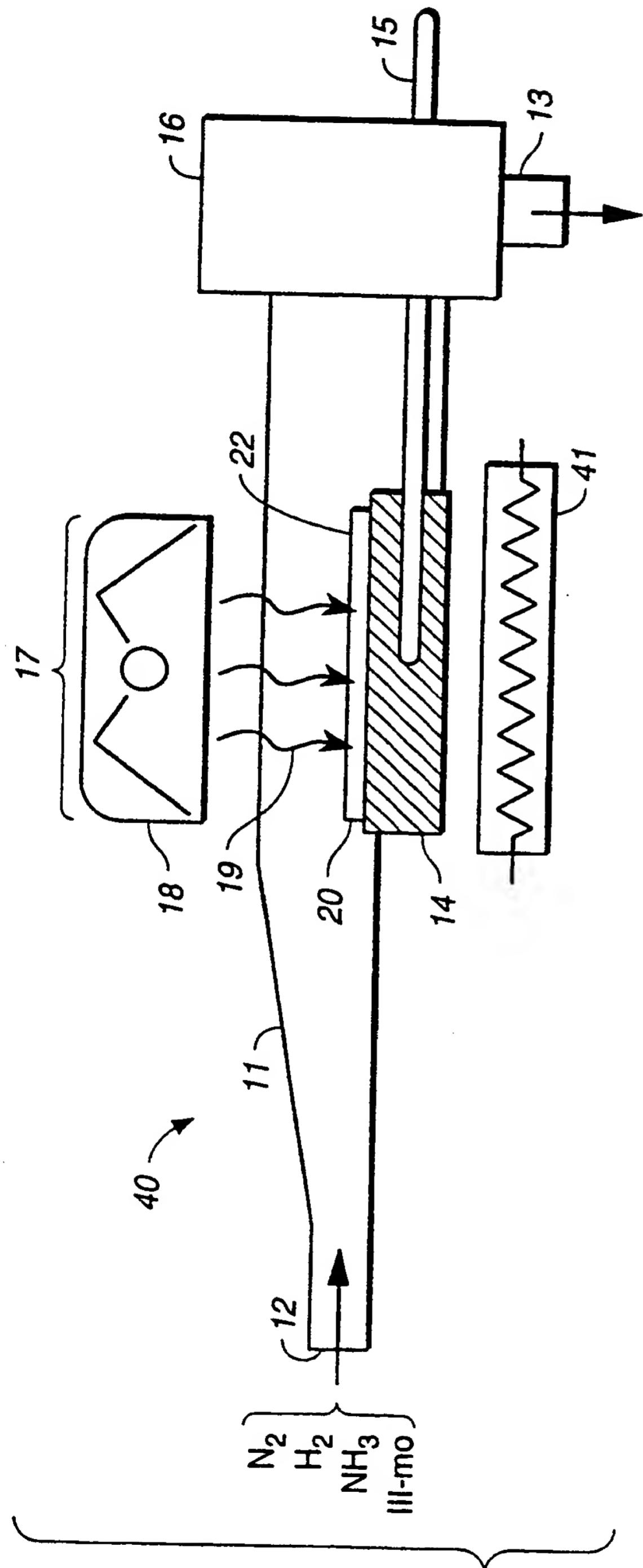


FIG. 2

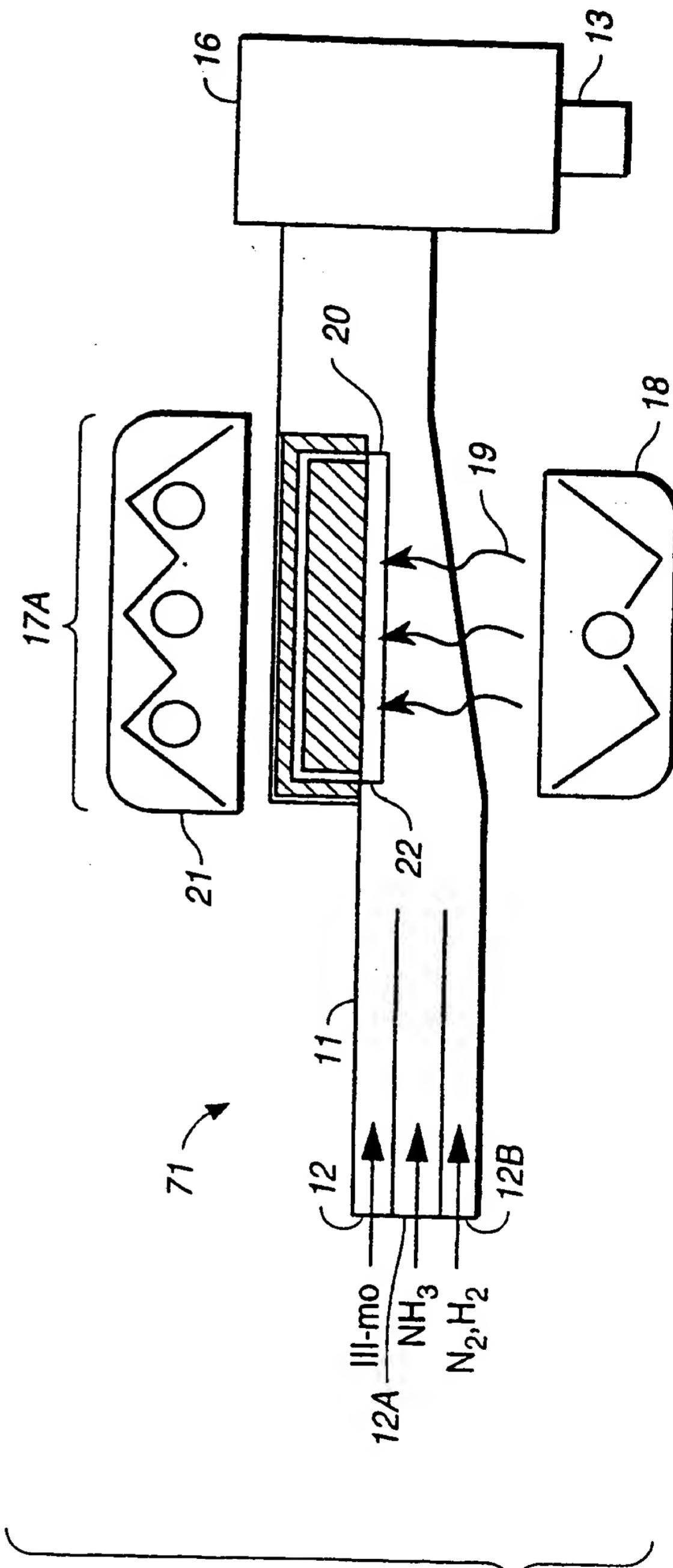


FIG. 3

3 / 9

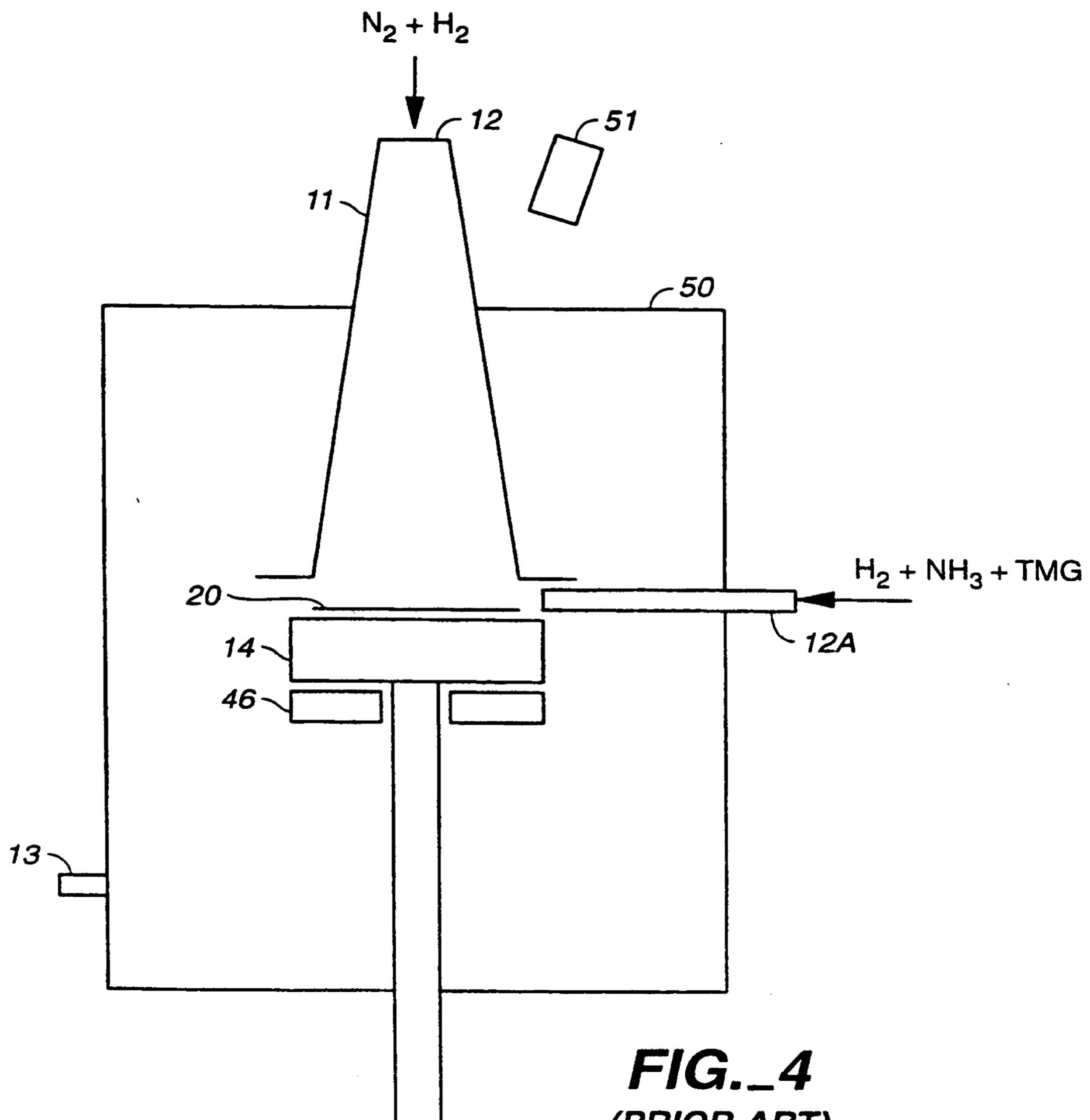


FIG._4
(PRIOR ART)

4 / 9

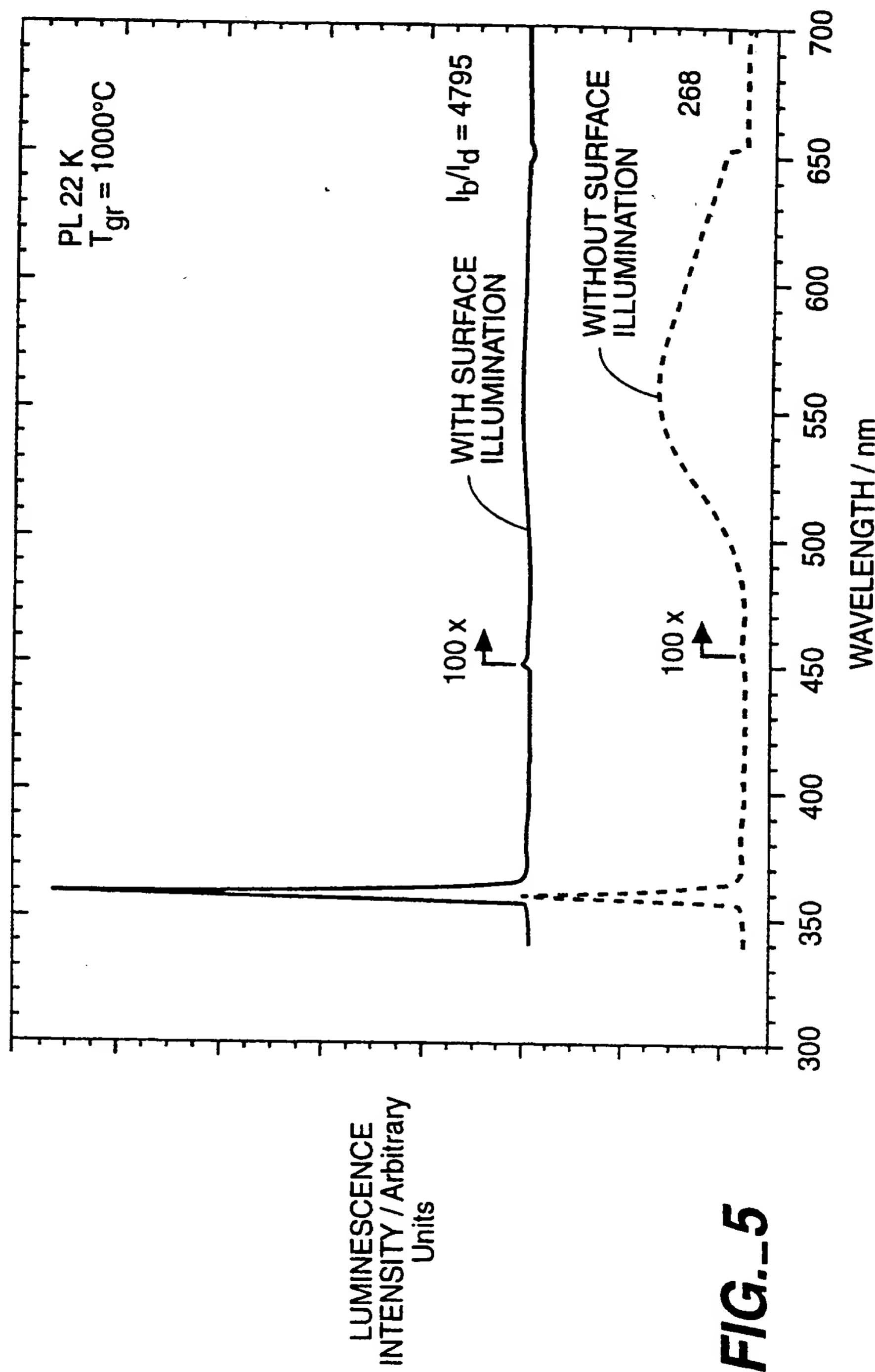
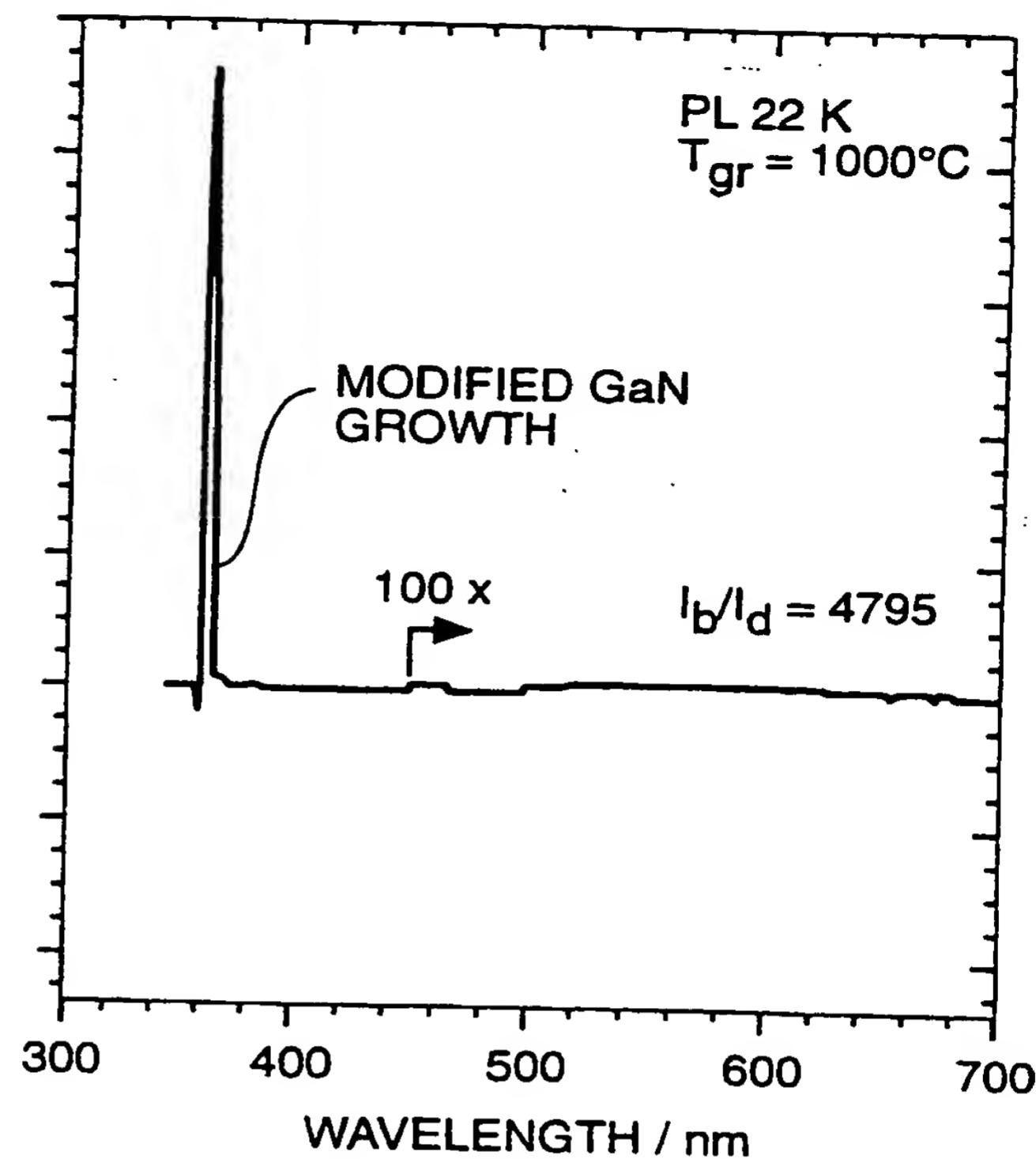
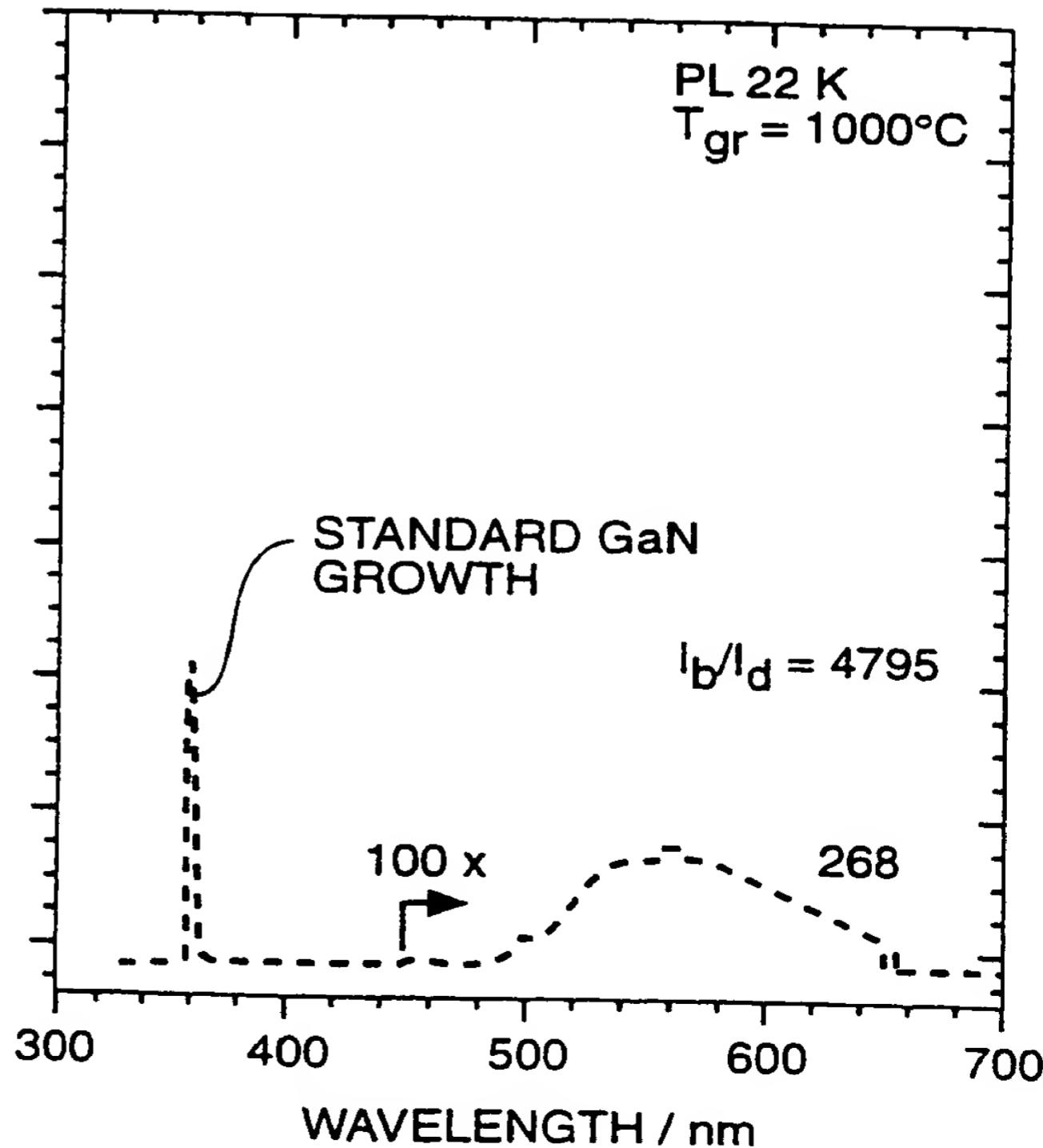


FIG. 5

5 / 9

INTENSITY / Arbitrary
Units**FIG._6A**INTENSITY / Arbitrary
Units**FIG._6B**

6 / 9

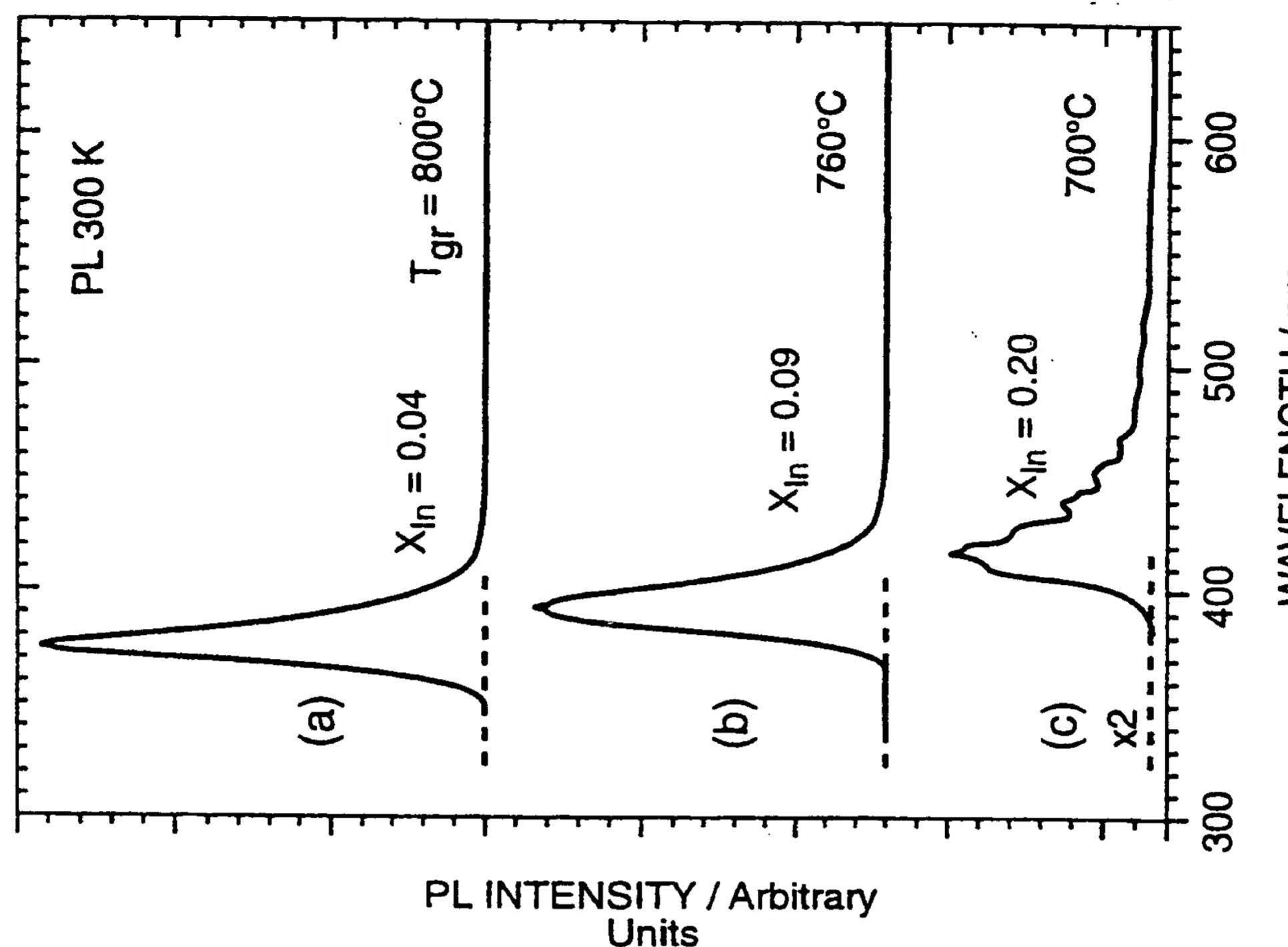


FIG._7B

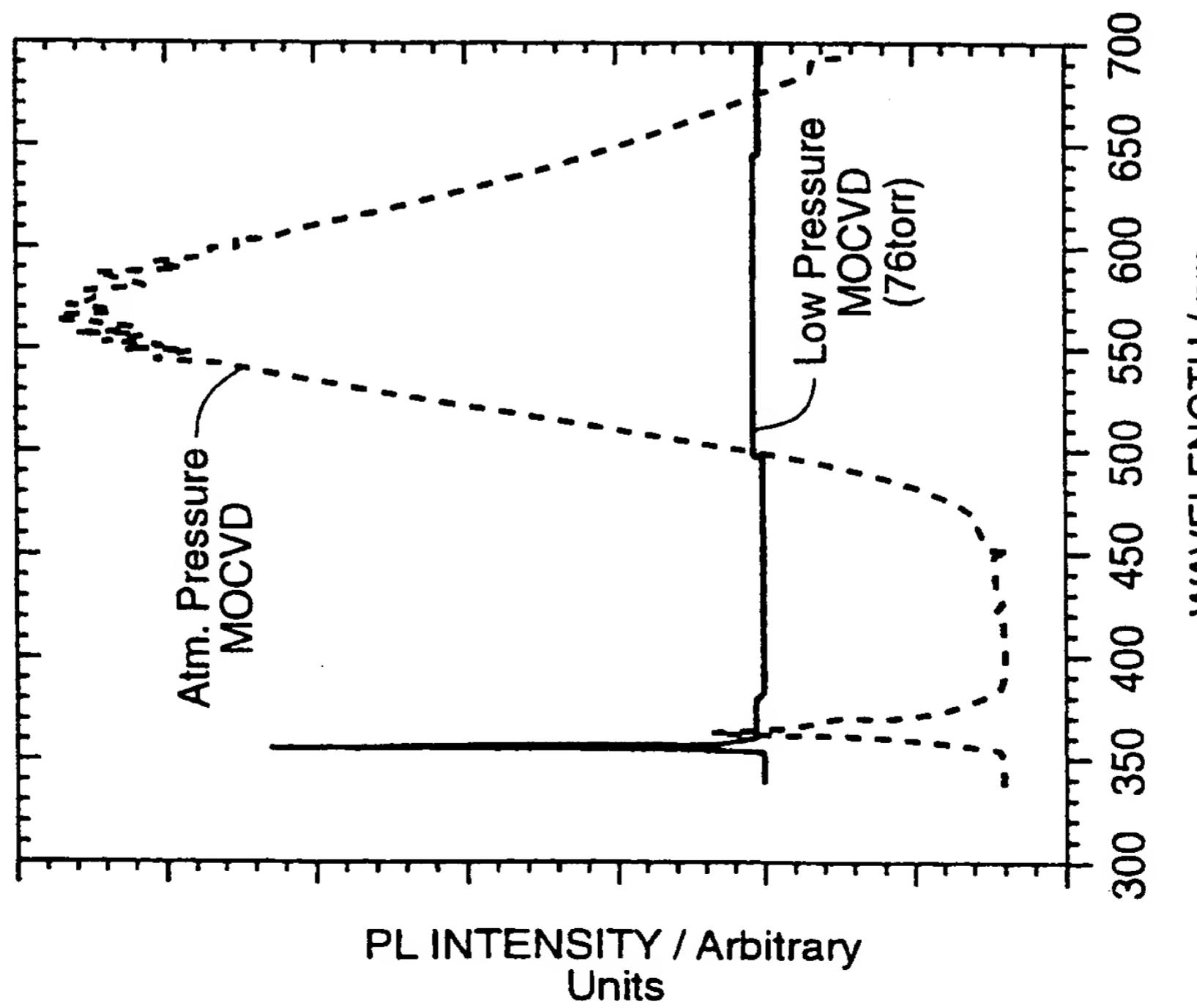
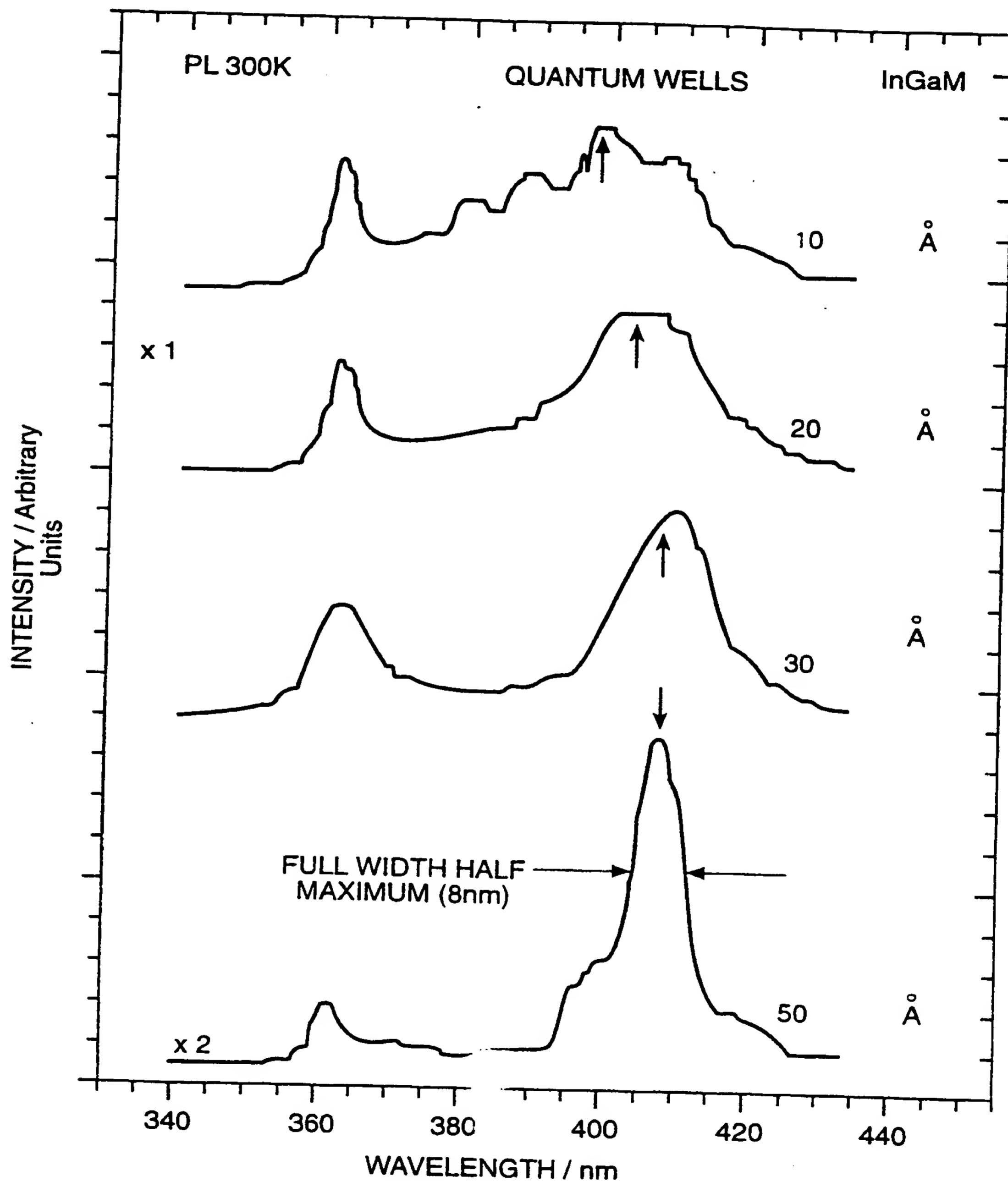


FIG._7A

7 / 9

**FIG._8**

8 / 9

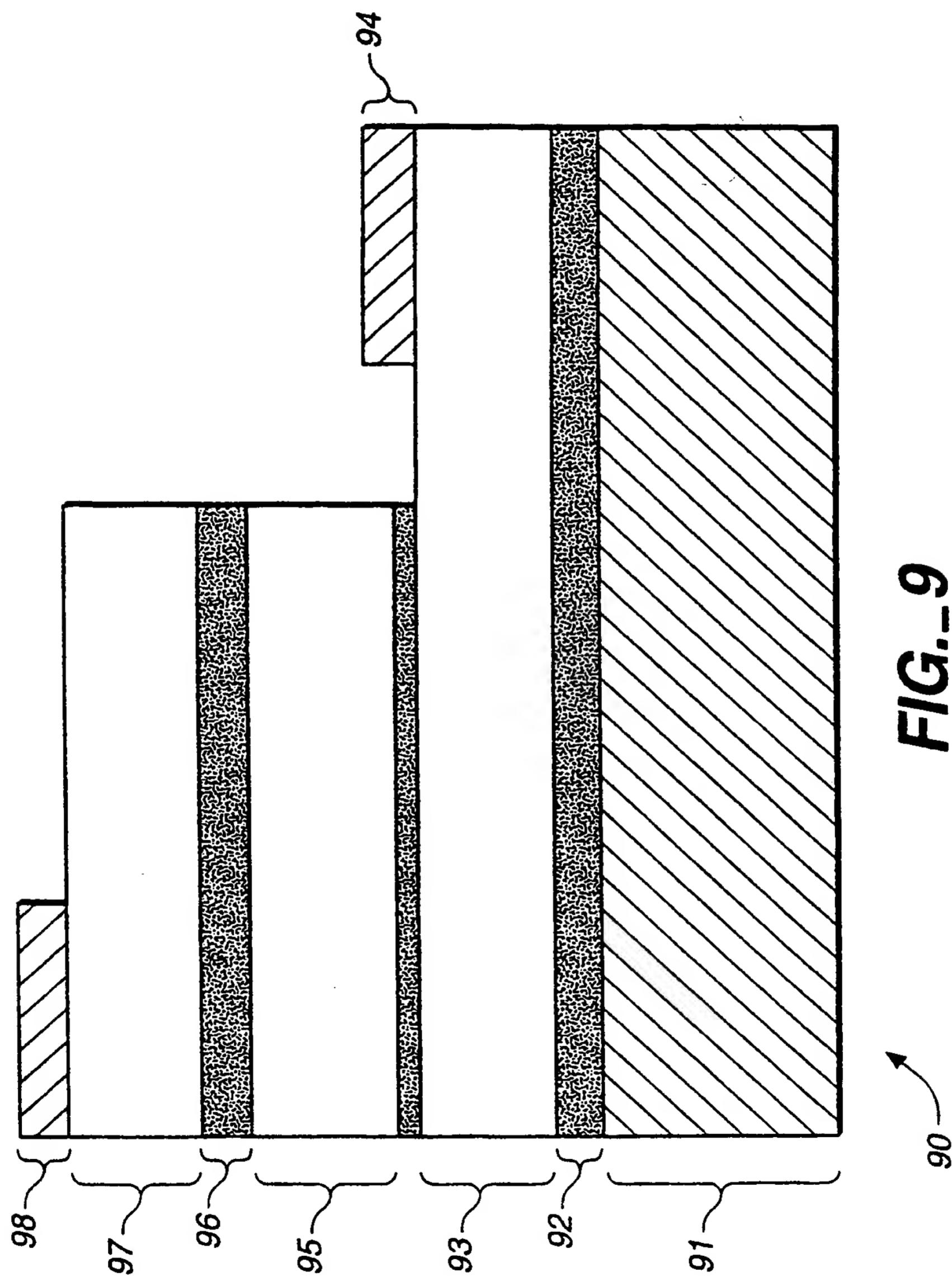
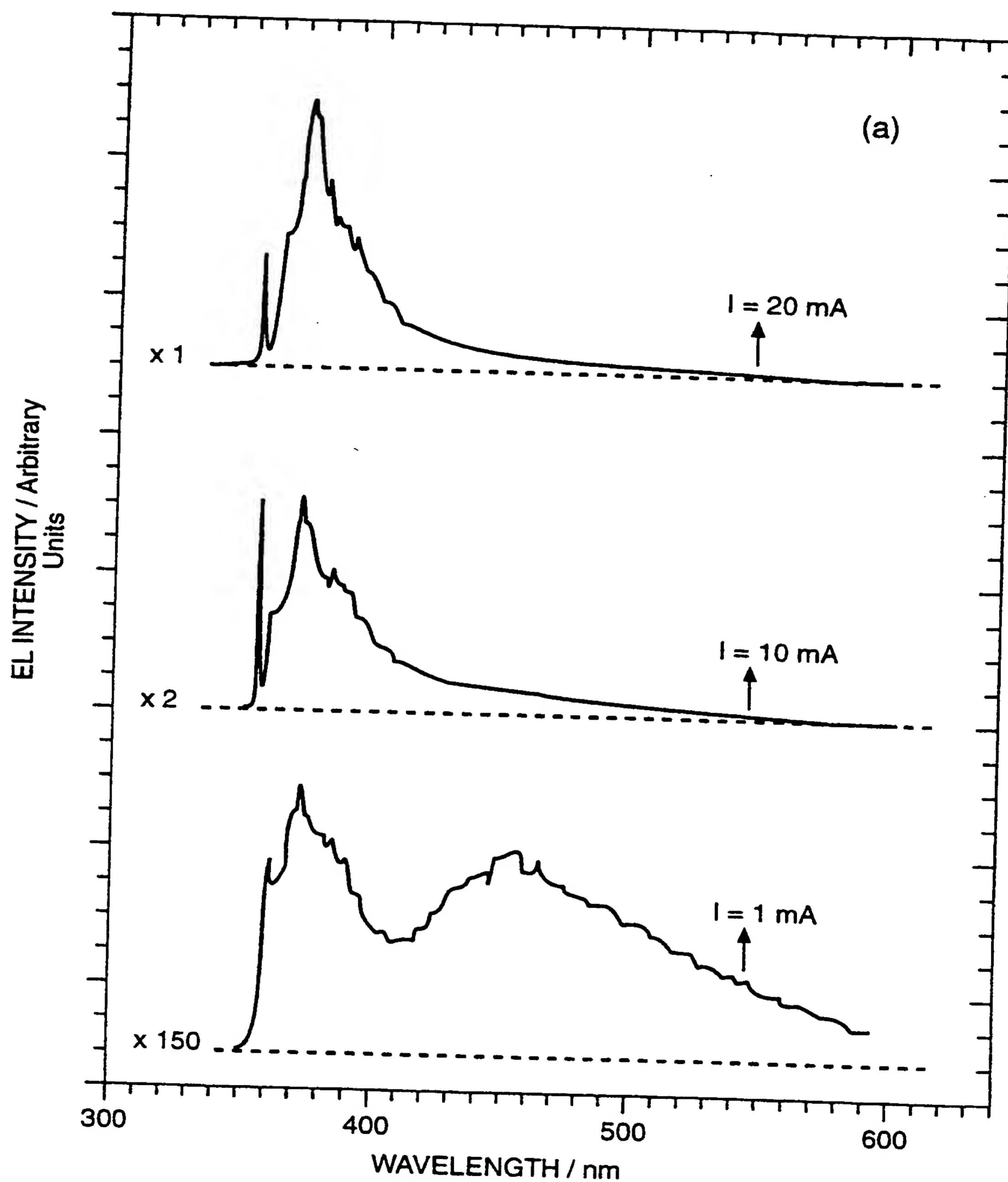


FIG. 9

9 / 9

**FIG._10**

3 Seite 4
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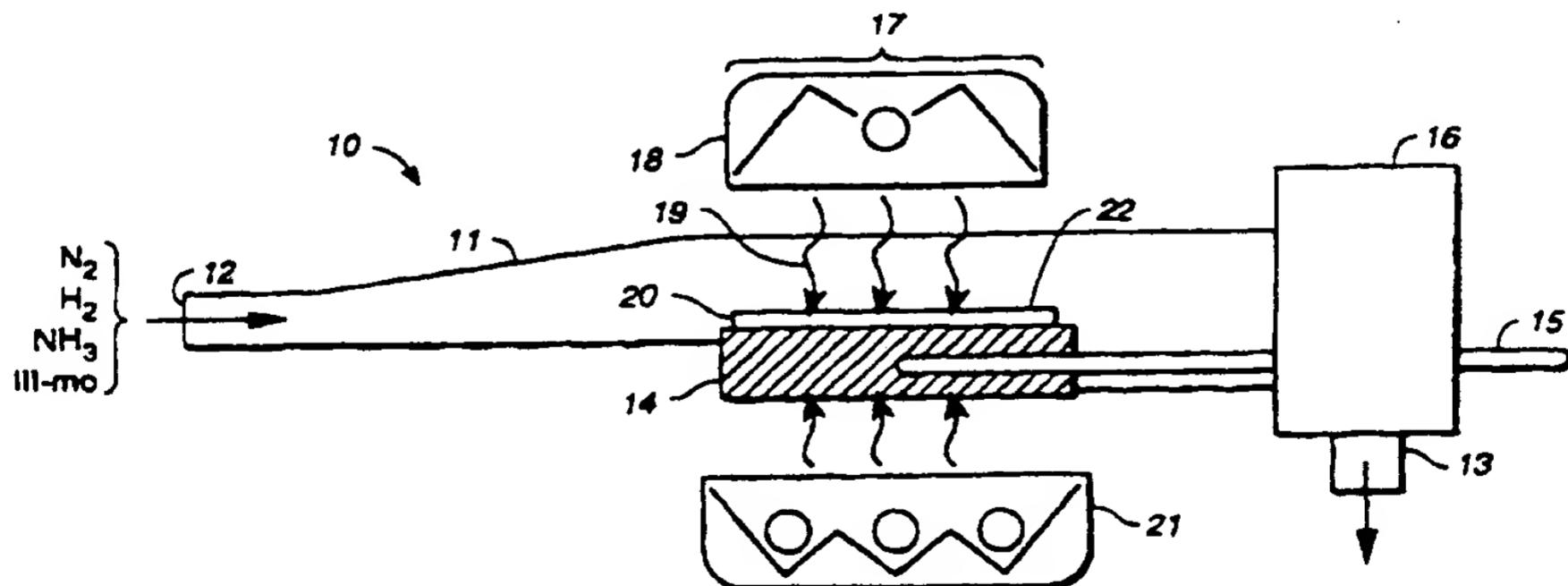
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :	A3	(11) International Publication Number:	WO 97/08356
C23C 16/00		(43) International Publication Date:	6 March 1997 (06.03.97)
(21) International Application Number:		PCT/US96/13188	
(22) International Filing Date:		16 August 1996 (16.08.96)	
(30) Priority Data:	US	(74) Agents:	PETERS, Howard, M. et al.; Peters Verny Jones & Biksa, L.L.P., Suite 6, 385 Sherman Avenue, Palo Alto, CA 94306-1840 (US).
08/516,527	18 August 1995 (18.08.95)	(81) Designated States:	JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(60) Parent Application or Grant		Published	
(63) Related by Continuation		With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
US		08/516,527 (CIP)	
Filed on		18 August 1995 (18.08.95)	
(71) Applicant (for all designated States except US): THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 22nd floor, 300 Lakeside Drive, Oakland, CA 94612-3550 (US).		(88) Date of publication of the international search report: 24 April 1997 (24.04.97)	
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(54) Title: MODIFIED METALORGANIC CHEMICAL VAPOR DEPOSITION OF GROUP III-V THIN LAYERS



(57) Abstract

An improved MOCVD apparatus (10) comprising an infrared transparent reactor (11) comprised of quartz or other material capable of withstanding pressures between about 1 and 10,000 torr, and a temperature between about 0 and 1500 degrees C. The reactor has an inlet port (12) for at least one volatile metalorganic compound, an inlet port (12) for a nitrogen containing gas, an outlet port (13), and a reaction zone (17) for growing a metal III nitride layer on a substrate (20) held by a susceptor (14). An infrared radiation source (18) is positioned immediately outside the reactor (11) for irradiating the growth surface (22) of the substrate (20), and a radiant heat source (21) is provided to heat the susceptor (14). The apparatus (10) produces films with useful properties by providing better control of nitride thin film formation, and is amenable to mechanization for less expensive mass production of films. The films are useful as semiconductors including LED devices.

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